UNIVERSITI PUTRA MALAYSIA

PREPARATION OF METHYL ACRYLATE-GRAFTED OIL PALM EMPTY FRUIT BUNCH FIBER AND ITS APPLICATION AS A FILLER IN POLY(VINYL CHLORIDE)/EPOXIDISED NATURAL RUBBER COMPOSITES

GUNASUNDERI RAJU.

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By

GUNASUNDERI RAJU

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfillment of the Requirement for the Degree of Master of Science

December 2005

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION OF METHYL ACRYLATE-GRAFTED OIL PALM EMPTY FRUIT BUNCH FIBER AND ITS APPLICATION AS A FILLER IN POLY(VINYL CHLORIDE)/EPOXIDISED NATURAL RUBBER COMPOSITES

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GUNASUNDERI RAJU

December 2005

Chairman : Professor Wan Md Zin Wan Yunus, PhD

Faculty : Science

Graft copolymerization of methyl acrylate (MA) onto OPEFB fiber has been successfully carried out using hydrogen peroxide and ferrous ammonium sulfate as initiators in an aqueous medium. The effects of reaction temperature, reaction period and amount of monomer and initiators on the percentage of grafting were investigated. The results show that the percentage of grafting depends on reaction period and temperature as well as concentration of monomers and initiators. The maximum percentage of grafting was obtained when the reaction was carried out using 33.36 mmol of MA, 6.00 mmol of H_2O_2 and 0.191 mmol of Fe^{2+} for 210 minutes at 75°C. The presence of the functional group in the grafted polymers was characterized by FTIR spectroscopy. Scanning electron microscopy was used to study the surface morphology. Thermogravimetric analysis indicated that the grafted OPEFB is thermally stable than the virgin OPEFB.

Effect of oil palm empty fruit bunch (OPEFB) fiber and poly(methyl acrylate) grafted OPEFB on several mechanical properties of poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) 50/50 and 70/30 blends were also studied. The

composites were prepared by mixing the fiber and the PVC/ENR blend using HAKEE Rheomixer at the rotor speed of 50 rpm, mixing temperature 150°C and mixing period of 20 minutes. The fiber loadings were varied from 0 to 30% and the effect of fiber content in the composites on their tensile strength (Ts), Young's Modulus, Modulus at 100% (M_{100}), elongation at break (Eb), flexural modulus, hardness and impact strength were determined. An increasing trend was observed in the tensile strength, Young's Modulus, flexural modulus, impact and hardness with the addition of grafted and ungrafted fiber to the PVC/ENR blend. A higher elongation at break and tensile strength and decrease in the flexural and Young's modulus observed with the addition of PMA-g-OPEFB fiber compared to ungrafted fiber. This observation indicates that grafting of PMA onto OPEFB impart some flexibility to the blend. Scanning electron microscope confirms that the increase in properties is caused by improved fiber-matrix adhesion. There was less inclination for the fibers to pull out of the matrix. Furthermore the thermal analysis by Dynamic Mechanical Analysis (DMA) indicated shifting in the Tg of the PVC/ENR composites with the addition of the OPEFB fiber. Thermogravemetric analysis (TGA) did not show any significant changes in the thermal stability. FTIR spectrums for the grafted and ungrafted fiber composites were almost identical.

Effect of electron beam radiation on the tensile properties of the PVC/ENR composites with 10% of fiber loading was studied. Electron beam irradiation and addition of crosslinking agent cause enhancement in tensile strength, Young's Modulus, Modulus at 100% (M_{100}) and gel content, with a concurrent reduction in the elongation at break (Eb) of the PVC/ENR composite.

Abstrak thesis yang dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN GENTIAN TANDAN KOSONG BUAH KELAPA SAWIT TERCANGKUK POLI(METIL AKRILAT) DAN APLIKASINYA DALAM KOMPOSIT ADUNAN POLI(VINIL KLORIDA)/GETAH ASLI TEREPOKSIDA

Oleh

GUNASUNDERI RAJU

Disember 2005

Pengerusi : Profesor Wan Md Zin Wan Yunus, PhD

Fakulti : Sains

Pempolimeran cangkuk metil akrilat ke atas gentian OPEFB dengan menggunakan hidrogen peroksida dan ferrus ammonium sulfat sebagai pemula dalam larutan akueus telah dikaji. Penyediaan dilakukan dengan kaedah pempolimeran radikal bebas. Daripada kajian ini didapati bahawa peratus pencangkukan metil akrilat ke atas gentian OPEFB bergantung kepada suhu tindak balas, jangkamasa tindak balas, kepekatan metil akrilat, kepekatan hidrogen peroksida dan kepekatan ferrus ammonium sulfat. Kajian ini menunjukkan keadaan optimum bagi pempolimeran cangkuk metil akrilat ke atas gentian OPEFB adalah pada suhu 75°C dan masa 210 minit dengan amaun MA, 33.36 mmol, H_2O_2, 6.00 mmol dan Fe^{2+}, 0.191 mmol masing-masing. Selain itu kehadiran kumpulan berfungsi yang dikesan oleh FTIR dalam OPEFB-g-PMA membuktikan bahawa pencangkukan telah berlaku. SEM telah di gunakan untuk melihat perbezaan di antara permukaan gentian OPEFB yang telah dicangkuk dengan yang tidak dicangkuk. TGA menunjukkan bahawa OPEFB yang telah dicangkuk adalah lebih stabil berbanding OPEFB asal.

Kesan penambahan gentian OPEFB dan gentian OPEFB yang telah dicangkukkan dengan poli (metil akrilat) terhadap sifat mekanikal adunan 50/50 dan 70/30 polivinil klorida/getah asli terepoksida (PVC/ENR) telah dikaji. Komposit adunan PVC/ENR yang mengandungi 0 hingga 30 % OPEFB telah disediakan dengan menggunakan pencampur dalaman HAKEE pada suhu 150°C, masa campuran 20 minit, dan kelajuan rotor 50 rpm. Perubahan dalam kekuatan tegangan, modulus Young, pemanjangan pada takat putus, modulus keterlenturan, kekerasan dan kekuatan hentaman dengan penambahan gentian OPEFB telah dikaji. Keputusan menunjukkan terdapat peningkatan dalam kekuatan tegangan, pemanjangan pada takat putus dan penurunan dalam modulus keterlenturan dan modulus Young untuk komposit gentian yang telah diubahsuai permukaannya degan yang tidak diubahsuai. Ini menunjukkan bahawa pengubahsuaian gentian OPEFB dengan PMA menambahkan keanjalan komposit tersebut. SEM telah digunakan untuk mengkaji permukaan retakan komposit PVC/ENR yang diperolehi daripada ujian kekuatan tegangan dan juga sample yang dipatahkan pada suhu cecair nitrogen. Ujian DMA mengesahkan bahawa Tg untuk adunan PVC/ENR teranjak dengan kehadiran gentian. TGA tidak menunjukkan sebarang perubahan manakala FTIR telah digunakan untuk mencirikan ikatan baru yang terbentuk.

Kesan sinaran alur elektron dan penambahan agen taut silang terhadap sifat-sifat tensil komposit PVC/ENR telah dikaji. Penyinaran komposit PVC/ENR 10% gentian memberikan sedikit kesan terhadap sifat mekanikal. Secara keseluruhan kekuatan tegangan, modulus Young, dan M_{100} meningkat manakala pemanjangan pada takat putus menurun dengan dos sinaran. Ujian kandungan gel telah membuktikan kewujudan taut silang akibat penyinaran dan penambahan agen taut silang.

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Finally, I thank God for His mercy and blessing on me.

Special Dedication

This thesis is specially dedicated to :

My parents who are infinitely precious to me.

My brothers Gunaselan and Gunasegaran and my sister in law who have filled my life with joy and happiness.

Prof Dr Wan Md Zin Wan Yunus

&

Dr Chantara Thevy Ratnam

To whom I am deeply grateful.

I certify that an Examination Committee met on 23rd December 2005 to conduct the final examination of Gunasunderi Raju on her Master of Science thesis entitled "Preparation of Methyl Acrylate-Grafted Oil Palm Empty Fruit Bunch Fiber and its Application as a Filler in Poly(Vinyl Chloride)/Epoxidised Natural Rubber Composites" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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Date: 27 MAR 2006

This thesis is submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the Degree of Master of Science. The members of the Supervisory Committee are as follows:

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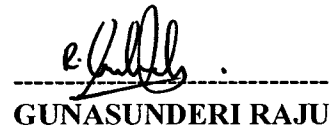
Date: 13 APR 2006

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other Institutions.



GUNASUNDERI RAJU

Date: 20/3/06

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LIST OF ABBREVIATIONS

ASTM	American Standard of Testing Materials
DMA	Dynamic Mechanical Analysis
DTG	Differential Thermogravimetry
E'	Storage Modulus
E"	Loss Modulus
EB	Electron Beam
Eb	Elongation at Break
EBM	Electron Beam Machine
ENR	Epoxidized Natural Rubber
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared
kGy	Kilo Gray
MPa	Mega Pascal
OPEFB	Oil Palm Empty Fruit Bunch Fiber
PMA	Poly(methyl) acrylate
PVC	Polyvinyl Chloride
rpm	Revolution per Minute
SEM	Scanning Electron Microscope
Tan δ	Tangent delta
Tg	Glass Transition Temperature
TGA	Thermogravimetric Analysis
TP	Thermoplastic
TPE	Thermoplastic Elastomers
TS	Tensile Strength
TPGDA	Tripropylene Glycol Diacrylate

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In recent years there has been increasing demand for new materials with friendly environmental impact. This demand has led to great interest in the plant derived materials such as natural fibers as the raw material for the production of conventional and advanced polymer materials.

The use of natural fibers as reinforcement or filler in the manufacture of fiber thermoplastic elastomer composites has been of great interest to many researchers. Natural fiber offers several advantages over inorganic fillers with regard to their lower density, high specific strength and modulus, less abrasiveness to processing equipment, wide availability, environmentally friendly, biodegradability and lower cost. The disadvantages of natural fibers in composites are the lower processing temperature, poor resistance to moisture and incompatibility with hydrophobic polymers. In order to enhance the compatibility between the fiber and the polymer involved, several techniques have been practiced. Among those often attract the interest of researchers in the field include surface modification of fiber, addition of coupling agents and compatibilizers.

Surface modification of natural fiber by graft copolymerization is one of the most widely used techniques. Graft copolymerization of vinyl monomers onto lignocellulosic is a promising method for modifying physico-chemical properties of

the natural fiber with the retention of the desirable properties (Xue and Wilkie 1997). Graft copolymerization helps in achieving specifically designed polymers properties by connecting different types of polymer having the desired properties onto the main chain (Lee and Lee 1997). Those properties include water absorbency, elasticity, ion exchanger capabilities, thermal resistance and resistance to microbiological attack can be enhanced by grafting (Mcdowall *et al.*, 1984).

The fiber reinforced polymers can be modified by using high energy electron beam irradiation. This technique has the ability to process materials at ambient temperature, fast processing rate and also to crosslink one of the polymers. Electron beam processing uses high energy electrons from an accelerator to initiate crosslinking reactions in suitable matrices thus improving their physical and chemical properties (Ratnam *et al.*, 2001).

In Malaysia oil palm empty fruit bunch (OPEFB) fiber waste is produced in millions of tonnes every year and can lead to unhealthy environmental impact. Oil palm empty fruit bunch (OPEFB) fiber is an important type of fibrous material left in the palm oil mill. It is obtained after the removal of oil seeds from fruit bunch for oil extraction and extracted by the retting process of the empty fruit bunch. OPEFB is an important lignocellulosic raw material which can be used for the preparation of cost effective and environmental friendly composite material. The total cellulose content (holocellulose) of the fiber was found to be 65% and 19% of lignin (Sreekala *et al.*, 2000). It was also found to have very low ash content. These factors contribute to better performance of the fiber as a reinforcement agent in polymers.

1.2 General Background

1.2.1 Copolymers

When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer. Monomer units can be arranged as shown in Figure 1 in a random, graft, block, and in an alternating fashions.

AABBBAABABBAAABB

Random

A-A-A-A-A-A-A-A-A-A-A
|
B
|
B-B-B-B
|
B

Graft

AAAABBBBAAAABBBB

Block

ABABABABABABABABA

Alternating

Figure 1: Monomer units arrangement in a copolymer

The properties of copolymers of A units and B units are influenced by the number the nature of the A and B units and by the length and arrangement of these units in the polymer chain (Sperling, 1974).

1.2.2 Graft Copolymerisation

Graft copolymers are branched molecular structures. The main polymer chain contains a side chain or graft of a different chemical nature (Figure 2).

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The initial step in graft copolymerisation involves the generation of a reactive radical site on the polymer backbone, followed by addition to an unsaturated monomer thereby yielding a graft copolymer.

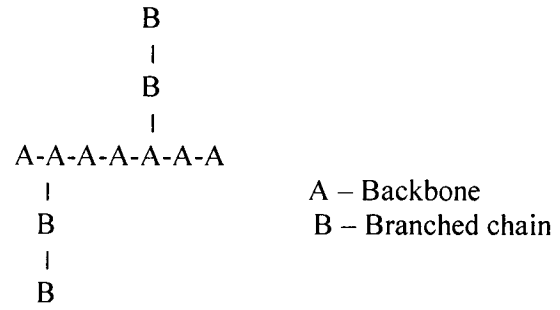

Figure 2: Structure of a graft copolymer.

Graft copolymers are generally prepared by free radical, anionic or cationic polymerisation (Noshay and James 1977). Most of the grafted copolymers are formed by free radical polymerisation which the major reaction is the chain transfer to polymer which involves abstraction of hydrogen atom. The reactivity of a free radical could be transferred to another species that enable to continue the chain reaction (BillMeyer, 1971). Grafting efficiency and grafting yield are strongly affected by the free radical source (Sperling, 1974).

1.2.3 Thermoplastics

A thermoplastics is a plastic that softens when heated and hardens again when cooled. Thermoplastics can generally go through many melt/freeze cycles with no appreciable chemical change, making them suitable for recycling. Thermoplastics offer many advantages over traditional materials, including: low density; low energy for manufacture; low processing costs; and the ability to make complex shapes relatively easily. Thermoplastic materials generally fall within two classes of molecular arrangement, amorphous (Figure 3) and semi-crystalline (Figure 4).

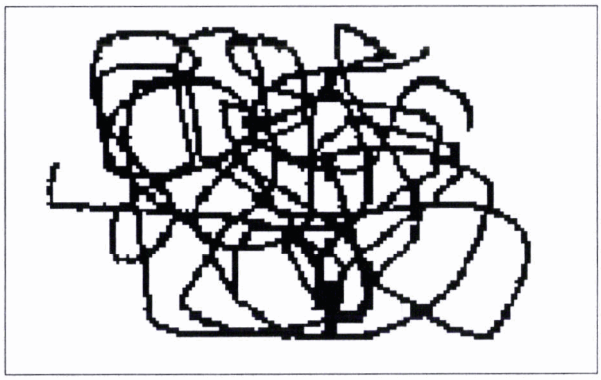

Figure 3: Amorphous

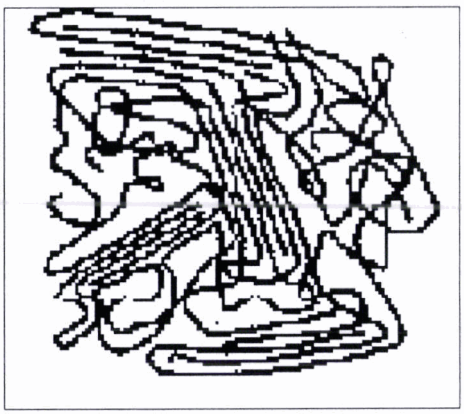

Figure 4: Semi Crystalline

1.2.4 Elastomers

An elastomer is a material that has significant elastic qualities. Elastomers are long polymer chains above their glass transition temperature. It is a synthetic rubber that can be stretched to at least three times its original length. Once the exerted pull force is released, it returns to its original length. Elastomers are usually lightly crosslinked and are easily deformed (Figure 5).

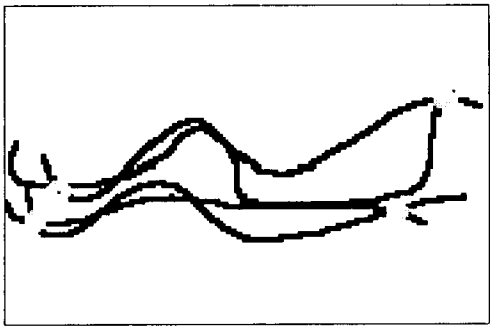

Figure 5: Elastomer

1.2.5 Thermoplastic Elastomer

Thermoplastic Rubber or Elastomer (TPEs) is a polymer blend or compound which above its melt temperature, have the elastic behaviour of rubber and the processability of thermoplastics. This process is reversible and the products can be reprocessed and remolded. Thermoplastic elastomers have two big advantages over the conventional thermoset (vulcanized) types. It is the processing ease and speed. The TPEs are molded or extruded on standard plastics-processing equipment in considerably shorter cycle times than those required for compression or transfer molding of conventional rubbers.